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LABORATORY OF PETROLEUM CHEMISTRY

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This laboratory was established in 1958 to promote the basic researches in the field of petroleum chemistry. In 1967, Dr. Okano succeeded Dr. Ichikawa as the head of the Laboratory. The present research subjects are organic synthesis using inorganic metal salts and organometallic compounds, the chemistry of reactive species having α-hetero atoms, and organic reactions in specific solvents. The synthesis of new monomers and polymers has also been undertaken. The researches have been developed by the present laboratory staffs (Drs. M. Okano, S. Tanimoto, S. Uemura, and T. Sugimoto) and their coworkers. In the following, the main results of these works are summarized.

I. Selective Halogenation and Other Reactions Using Inorganic Metal Salts

In contrast to the well-known *trans*-addition of halogens to olefins, $SbCl_5$ and $MoCl_5$ were found to be good *cis*-chlorinating reagents for simple olefins. Alkylphenylacetylenes similarly reacted with $SbCl_5$ to afford *cis*-dichloroolefins predominantly, while with $CuCl_2$ the *trans*-isomers were formed with a high selectivity. The mixed halogenations of olefins and acetylenes by equimolar mixtures of $SbCl_5$ and halogens (Br_2 or I_2) or metal halides (LiBr or LiI) occurred with ease in the *trans* manner. Highly selective *p*-halogenations of halobenzenes were also achieved by the use of these mixtures. A mixture of $SbCl_5$ and $Pb(SCN)_2$ was found to be a good reagent for aromatic thiocyanation. Several new aspects in the chlorinations of cyclic dienes and norbornene with various metal chlorides were elucidated. Some oxidation reactions by Fe(III) and Tl(III) salts were also studied.

II. Synthesis via Organothallium(III) Compounds

The earlier project planned by Dr. Ichikawa, the former head of this Laboratory, was partly succeeded and has been developed by one of the staffs (S.U.) in the field of the chemistry of organothallium(III) compounds.

In collaboration with Dr. Ichikawa's group, it was found that arylthallium(III) compounds react with copper(I or II) halides or pseudohalides to give halo- or pseudohaloarenes, the substitution occurring at the *ipso* position. Since the thallation of arenes occurs with a high selectivity, this reaction may provide a new route for the introduction of a halogen or pseudohalogen into the selective position of the aromatic nucleus. The reaction was found to be also applicable to the oxythallates of olefins and acetylenes.

The acetoxythallation of alkylphenylacetylenes and the proto- and halodethalla-

tions of the products were studied, emphasis being placed on their stereochemistry. A new type of oxythallation adduct was obtained from terminal acetylenes.

The reactions of arylthallium (III) compounds with $NaNO_2$ and $PdCl_2$, and those of oxythallates with $PdCl_2$ and $NaBH_4$ were also studied.

III. Chemistry of Some Reactive Species Having α-Hetero Atoms

The behavior of some unfamiliar carboxylic acid derivatives has been examined. N,N-dialkylformamide dichlorides showed a high reactivity toward various unsaturated bonds, such as C=N, N=S, and activated C=C, the 1 : 1 adducts being formed. N,N-dialkylformamide dialkylacetals reacted more readily with Grignard reagents than orthoformates. The reaction of isocyanide dichlorides, an analog of phosgene, with Grignard reagents yielded α-elimination products rather than substitution ones. The Cl atom in β-chloro- or β,β-dichlorovinylsulfones was less effective than that in β-chlorovinylketones.

The chemistry of $\rangle N\text{-}CH_2\text{-}S\text{-}$ and $\rangle \overset{+}{N}\text{-}CH_2\text{-}\overset{+}{S}\langle$ types of compounds has also been studied. The SO_3Na group in (N-sulfomethyl)anilide and -benzamide was readily replaced by amide groups. In (sulfonio)methylammonium salts, the displacement of the sulfide moiety by an amine or phosphine molecule occurred smoothly. The H-D exchange in the dionium salts was observed near pH 5.

IV. Reactions in Specific Solvents and Reactions Involving Solvent Incorporation

By the use of polar aprotic solvents, the one-stage preparation of polysubstituted (chloro)ethylenes from polychloroalkanes and phenolate or thiophenolate anion was achieved. The reaction of secondary and tertiary alkyl halides with $Hg(SCN)_2$ in less-polar solvents afforded N-alkylation products predominantly, in contrast to the reaction with KSCN in polar aprotic solvents. A similar reaction in tetrahydrofuran produced the solvent-incorporated products. Based on this foundation, a convenient method to prepare 4-alkoxybutyl acetates and chlorides was developed. Similarly, the Lewis acid-catalyzed reaction of isocyanides and chlorine in tetrahydrofuran yielded 4-chlorobutyl carbamates. An example of the incorporation of another solvent was found when alkylbenzenes were treated with $TlCl_3 \cdot 4H_2O$ in carbon tetrachloride; the products were the corresponding benzoic acids, formed *via* benzotrichlorides, along with chlorinated aromatic compounds.

V. Synthesis of Monomers and Polymers, and Polymer Reactions

One of the staffs (S. T.) has been interested in studies of polymer synthesis as well as of organic synthesis.

A method for the preparation of *p*-chloromethylstyrene was offered. Several *p*-substituted styrenes, having a reactive functional group as the substituent, and some acrylic acid derivatives were prepared and the behaviors of their polymers were ex-

amined. A few representative results were given below. A cross-linked sulfonium salt type polymer, prepared from *p*-vinylphenyl methyl sulfide, was found to convert benzaldehyde into styrene oxide in the presence of a strong base, indicating the intermediate formation of a S-ylide polymer. The recovered polymer could be changed to the original one. A new type of epoxy resin was prepared by polymerization of *p*-vinylphenyl glycidyl ether. Polymerization of polychloroalkyl acrylates afforded flame-resistant films. By polycondensation reactions, new heat-resistant polymers, such as poly(amide-benzimidazoles), poly(amide-benzoxazoles) and poly(quinacridonequinone), were also prepared.

In addition, the Laboratory of Synthetic Rubber Chemistry (alias Oda Laboratory) was incorporated into this Laboratory after Dr. Okano became the head of the latter laboratory. In this field, studies on copolymerization reactions were actively carried out by Drs. Furukawa and Kobayashi. By the proper choice of catalysts, they succeeded in preparing commercially attractive copolymers, such as a butadiene-acrylonitrile alternating copolymer (a new synthetic rubber) and a butadiene-acetylene copolymer (a synthetic drying oil). Published papers on these studies are also included in the last part of the following publication list. Drs. Oda and Furukawa were retired from Kyoto University in 1970 and 1976, respectively.

Publications

(* indicates an article published in Japanse)

I. Selective Halogenation and Other Reactions Using Inorganic Metal Salts

(a) Halogenation with Metal Halides

1. S. Uemura, O. Sasaki, and M. Okano: Selective *cis*-Chlorination of Olefins by Antimony(V) Chloride, *Chem. Comm.*, **1971**, 1064.
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4. S. Uemura, A. Onoe, and M. Okano: Molybdenum(V) Chloride as a Reagent for *cis*-Chlorination of Olefins, *ibid.*, **47**, 3121 (1974).
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(b) Halogenation with Mixtures of Halogen Donors and Metal Halides

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12. A. Onoe, S. Uemura, and M. Okano: Alkoxythiocyanation and Alkoxyiodination of Olefins with Copper(II) Salts, *ibid.*, **47,** 2818 (1974).
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(c) Metal Salts-Catalyzed Reactions

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(d) Oxidation with Metal Salts

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II. Synthesis via Organothallium (III)Compounds

(a) Reactions of Arylthallium (III) Compounds

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(b) Synthesis and Reactions of Oxymetallated Compounds

8. S. Uemura, A. Tabata, and M. Okano: 1,2- and 1,4-Diacetoxylation of Conjugated Dienes with Thallium(III) and Lead(IV) Acetates, *Chem. Comm.*, **1970,** 1630.
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11. S. Uemura, K. Sohma, H. Tara, and M. Okano: Reaction of Alkylphenylacetylenes with Thallium (III) Acetate, *Chem. Letters,* **1973,** 545.
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5. N. Watanabe, S. Uemura, and M. Okano: The Reaction of Alkyl Halides with Mercuric Thiocyanate in Tetrahydrofuran. The Solvent Incorporation and the Intermediacy of O-Alkyltetrahydrofuranium Ions, *ibid.*, **48,** 3205 (1975).
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V. Synthesis of Monomers and Polymers, and Polymer Reactions

(a) Monomer Synthesis

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6. S. Tanimoto, R. Taniyasu, and M. Okano: The Synthesis of Several N,N'-Bis(hydroxymethyl) Parabanic Acid Derivatives, *Bull. Chem. Soc. Japan*, **48**, 357 (1975).

(b) Polymer Synthesis and Polymer Reactions

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VI. Miscellaneous

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5. S. Tanimoto and S. Yasuda: Synthesis of Some Chloroepoxides from α,β-Dichloropropionaldehyde, *ibid.*, **29**, 530 (1971).*
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VII. Reviews

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VIII. Copolymerization Reactions (Studied by Dr. Furukawa *et al.*)

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